Superconductivity of Bismuth, Barium, and Lead at Pressures Exceeding 100 Kbar

M. A. IL'INA, E. S. ITSKEVICH, AND E. M. DIZHUR

Institute of the Physics of High Pressures, USSR Academy of Sciences

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The $T_c(P)$ dependences are studied for the high-pressure modifications of bismuth, barium, and lead existing in the 100–200 kbar range.

THE study of the superconductivity of high-pressure phases of elements is of paramount interest for deepening our understanding of the superconducting state. Such investigations in the range of pressures above 100 kbar have already been carried out (see, for example,[1]). However, the limited number of laboratories where the investigations are conducted and their inadequate scope make every new attempt in this direction highly desirable.

We have used new methodological possibilities, which permit us to study the superconducting transition temperature T_c in a pressure range up to 200 kbar and measurements have been made on bismuth, barium, and lead.

METHODOLOGY

In 1969, Brandt and Berman reported the attainment of pressures up to 250 kbar by means of anvils of the Bridgman type at liquid helium temperatures.[2,3] In the same year, Gey and Eichler[4] reported an extension of the range to 300 kbar limiting pressure in the fixed-pressure chamber of Wittig;[5] however, they did not give any experimental data. The results of the experiments carried out by means of a chamber[3] have, as the authors themselves point out, an intrinsic error of ± 20 kbar at $P > 150$ kbar.

We used a high-pressure chamber of the Bridgman anvil type with an effective support of the high pressure cell developed by Vereshchagin, Novikov and Khvostantsev in our Institute and modified for operation at low temperature.[1)] The chamber was placed in a "cold" pressure booster, which permitted us to obtain the necessary force applied to a chamber maintained at the temperature of liquid helium.[6]

The high-pressure cell consisted of pyrophyllite disks, between which there were two samples in the form of flat strips, each of which was furnished with four electrodes.

The calibration of the chamber was carried out against the jumps in the electrical resistance at the phase transitions for bismuth, barium, and lead at room temperature. The pressures at the transitions was found by us to be: 59 kbar for Ba I–II, 89 kbar for Bi V–VI, 144 kbar for Ba III–IV, and 160 kbar (onset of the transition) and 180 kbar (end of the transition) for Pb I–II.

In each calibration experiment, we used two reference metals placed in two "stages" of the chamber. The plot of the dependence of the pressure in the chamber on the load was linear in the range 60–180 kbar.

The use of references in one of the stages in each experiment materially increased the accuracy of determination of the pressure in the chamber.

For the determination of the pressure gradient in the chamber, we performed two experiments with barium samples in each stage. It was found that a shift of one of the samples by ~1 mm from the center of the disk did not lead to any appreciable change in the load, which corresponds to the transition Ba III–Ba IV.

We estimate our maximum error in the pressure at ~3%.

The temperature above 4.2°K was obtained by us while heating the cold pressure booster above the level of liquid helium and was measured with an Allen-Bradley carbon thermometer. The heating was at a rate of about 0.01 deg/min.

The mean error in the values of the pressure and T_c, unless specially noted in the figures, lies within the dimensions of the points of the $T_c(P)$ plot.

a) Bismuth. Detailed studies of the $T_c(P)$ dependence for various modifications of bismuth were carried out by us previously[7] in the pressure range 0–100 kbar.

In the pressure range 100–200 kbar, the superconductivity of the bismuth was studied only by Berman.[8] The superconducting transition temperature T_c for bismuth was measured by him only for two pressures, 140 and 240 kbar. We carried out a more detailed investigation of T_c for bismuth in this same pressure range.

Figure 1 shows the obtained temperature dependence of the relative electrical resistance of the bismuth samples for various pressures.

Figure 2 shows the dependence of the transition tem-

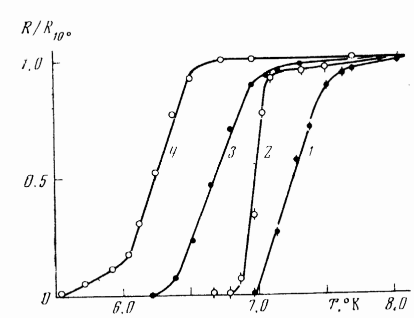


FIG. 1. Curves of the superconducting transition in bismuth at various pressures P (kbar): 1–153, 2–160, 3–170, 4–190.

[1)]The authors plan to publish a detailed description of this method separately.

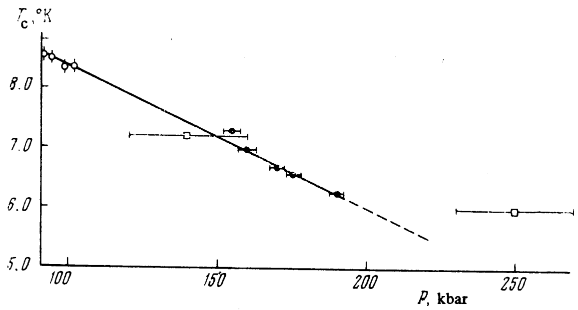
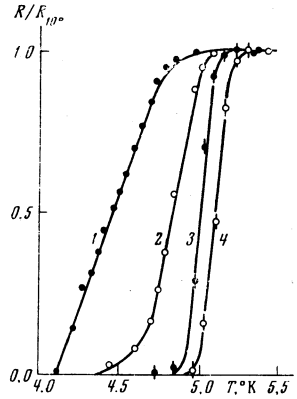


FIG. 2. Dependence of T_c(P) for the high pressure modification Bi IV: ○—data of [7], □—[8], ●—present work.



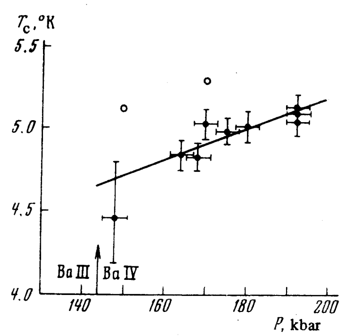


FIG. 3. Curves of the superconducting transitions in barium for various pressures P (kbar): 1–148, 2–168, 3–175, 4–192.

FIG. 4. Plot of T_c(P) for the high-pressure modification Ba IV: ○—data of [10], ●—present work.

perature T_c on the pressure for the Bi VI modification that exists in this pressure range. It is seen that the obtained critical temperatures fit very well on the extrapolation of the straight line with slope $dT_c/dP = -(2.3 \pm 0.5) \times 10^{-5}$ deg/bar (observed by us previously) into the region of higher pressures.[7] The excellent linearity of T_c(P) in the pressure range studied by us permits the hope that a pressure scale for low temperatures can be constructed in this pressure range by using bismuth. The point obtained by Berman[8] at 250 kbar does not fall on the extension of our curve (Fig. 2). We note that the pressure scale used by Berman was based, as was ours, on the value of the transition pressure of Pb I—Pb II, viz., 160 kbar.

b. Barium. The investigations of the superconductivity of barium in the range of pressures up to 100 kbar were described by us in[9]. The results obtained in the range of pressures above 100 kbar are shown in Figs. 3 and 4. In the pressure range up to 145 kbar, no singularities are observed on the $R(T)_{p=const}$ curves down to a temperature ~1.5°K, which indicates the absence of superconductivity of barium above 1.5°K and agrees with the negative slope of the T_c(P) curve obtained by us previously[9] for Ba III. Beginning with P = 150 kbar, discontinuities of the electrical resistance are observed on the $R(T)_{p=const}$ plots and accompany transitions to the superconducting state with T_c = 4.85°K at 164 kbar. Further increase of the pressure to ~200 kbar gives an increase in T_c with $dT_c/dP = +(1.3 \pm 0.5) \times 10^{-5}$ deg/bar.

An interesting feature of the superconducting transition of Ba IV is the significant dependence of the superconducting transition temperature T_c on the current in the sample at constant pressure.

An increase in the current by a factor of about 6 (from 7 to 40 mA) led to a decrease in the superconducting transition temperature T_c by ~0.4°K. This effect was not studied in more detail.

Points from the work of Wittig and Matthia[10] are plotted in Fig. 4, along with the experimental data obtained by us. These points lie about 0.4°K above our T_c(P) curve. The reason for such a discrepancy lies in the inaccuracy of the determination of both the temperature and the pressure by Wittig and Matthias.

The appearance of superconductivity in barium is related qualitatively by Gandel'man and Fedorov[11] to the change in the band structure under pressure.

Barium has partially filled 5d bands along with the 6s bands. As the pressure is increased the d bands, which lie above the Fermi surface at normal pressure, begin to descend and reach the Fermi surface. In turn, the s bands rise and approach the d bands, so that the s and d bands intersect in some pressure range. Electron rearrangement takes place, in which the electrons undergo transition from the s band to the unfilled d band.

With further compression, the s band becomes unfilled and is located above the d band.

Superconductivity under pressure can be understood from the viewpoint of the change in the band structure. Upon increase in pressure, the slightly filled d levels descend and begin to play the role of resonant ones. This affects the electron-ion scattering and leads to an increase in the matrix element of electron-phonon interaction. The result of this should be the appearance of superconductivity.

A natural experimental fact, which does not fit in the framework of these discussions, is the presence of the barium modification Ba III which exists in the range 85—145 kbar and has a negative dT_c/dP.

c) Lead. At a pressure of 160 kbar, lead transforms into a new crystallographic modification. The transition is accompanied by a rather clearly marked discontinuity in the electrical resistance.

The T_c(p) dependence was studied by Wittig over the entire range of existence of PbI up to 160 kbars.[5] The superconducting properties of the phase Pb II, which arises at a pressure >160 kbars, was studied by

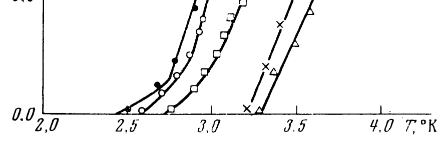


FIG. 5. Curves of the superconducting transition in lead at various pressures P (kbar): 1–200, 2–175, 3–168, 4–160, 5–135.

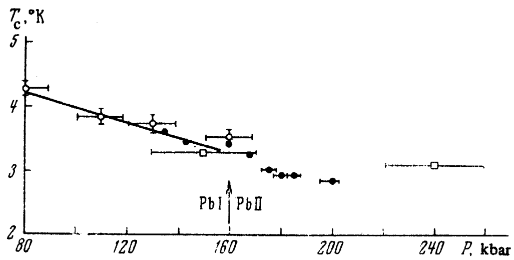


FIG. 6. Plot of $T_c(P)$ for lead: ○—data of [5], □—[8], ●—present work.

Berman.[8] The superconducting transition temperature T_c was measured by him at two pressures, 150 and 200 kbars.

We have carried out detailed studies of the temperature of the superconducting transition of lead as a function of pressure in the range 130—200 kbar.

Figure 5 shows the resultant temperature dependences of the reduced electrical resistance $R/R_{4.2°K}$ at various pressures for both modifications of lead. Figure 6 shows the pressure dependence of the superconducting transition temperature T_c in the pressure range 130—200 kbar. The data of Wittig[5] and Berman[8] are also plotted. In the range up to 160 kbar, our data are in excellent agreement with the data of Wittig[5] and as the phase transition temperature is approached the value of dT_c/dP is the same according to the data of both researches, $-(1.1 \pm 0.5) \times 10^{-5}$ deg/bar.

The accuracy of our experiments does not permit us to solve the problem of the presence and sign of the discontinuity of T_c in the transition to the new phase Pb II. However, in the region of the transition Pb I—Pb II, a definite change is observed in the value of dT_c/dP. In this range of pressures, for the phase Pb II, $dT_c/dP = -(2.2 \pm 0.5) \times 10^{-5}$ deg/bar. It is seen from Fig. 6 that Berman's point at 240 kbar[8] lies somewhat out of line with the extrapolation of our $T_c(P)$ curve.

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